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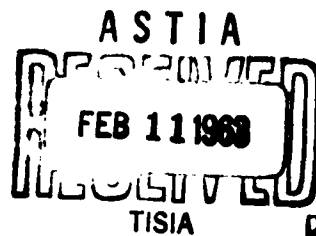
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THE ISOTOPIC EFFECT IN THE ELECTROSYNTHESIS
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In another work [1] the presence of an isotopic effect in the electrosynthesis of ozone was ascertained and its magnitude was determined. One and two-stage enrichment of ozone with the heavy isotope of oxygen was experimentally achieved.

We determined the separation coefficient and the nature of the isotopic effect in the electrosynthesis of ozone by methods differing in principle from those used in the other work [1] and providing repeated separation of the oxygen isotopes in an elementary compartment; regime in accordance with the Rayleigh conditions for exhaustion. This was attained by continuous circulation of the oxygen through the ozonizer in a closed circuit and by removing the ozone from the circulating stream by chemical absorption. The degree of the conversion of oxygen into ozone was assigned the limits of 45 to 90%. We evaluated the separation process as it was going on by measuring the isotopic composition of the oxygen in the residue. The value of the separation coefficient was determined for each single experiment with an error of 10-15%. The results of our experiments are found to be

in good accord with the data in the work cited [1].

Figure 1 represents the line diagram of the setup used for the research. The oxygen was moved through the closed circuit by centrifugal compressor 1 with a working pressure of 400 mm Hg, which is the maximum possible for compressors of this type. The setup provided a vacuum of 10^{-4} mm; and the centrifugal compressor, up to 10^{-5} mm, so that leakage of air into the setup practically did not occur.

From the compressor the gas entered ozonizer 2. After the ozonizer the oxygen-ozone mixture passed through the system of entrainment separators 3 filled with KI solution where absorption of the ozone took place. The gas was cleaned and dried in column system 4. Rheometer 5 determined the velocity of the gas and it was regulated by valve 8. Mercury manometer 6 measured pressure in the system. Drawing off the samples of oxygen for isotopic analysis took place through a sampler into flask 7 which had been pre-evacuated to $(1-2) \cdot 10^{-2}$ mm Hg.

A glass ozonizer was used in the experiments. The length of the reaction zone in the ozonizer was 600 mm and the width of the gas slot, 1.5 mm. The outside diameter of internal electrode 9 was 30 mm. Ozonizer volume was 84.9 cm^3. The ozonizer was powered by electric current from an NTGM-10 transformer by connecting one of its terminals to the ozonizer's internal electrode. The external electrode of the ozonizer and one of the transformer's terminals were grounded. The experiments were conducted at a potential difference of 15 kv, which guaranteed an electric field voltage of the order of 1000 v/cm at the slot. To prevent current leakage through the water used for cooling the ozonizer the pipes were made of glass tubing 12 m long with a resistance of 25 Mohm. The degree of the oxygen-ozone conversion was determined iodometrically and from the pressure drop in the system.

Before starting work the entrainment separators 3 were filled with a potassium iodide solution. The setup was evacuated to several mm Hg and exposed to flushing with oxygen and filling to 400 mm Hg. Then the compressor and high voltage were turned on. At the beginning of the experiment a volumetric velocity was ascertained equalling 4.5 l/min; it dropped in step with the conversion of oxygen into ozone. A certain degree of oxygen-ozone conversion p was reached, after which three oxygen samples of the same composition were extracted for isotopic analysis. The experiments were duplicated. The samples were isotopically analyzed on an MS-2 mass spectrometer by the ordinary method. Extraction of samples took place after each experiment.

Determination of the value of the separation coefficient was done in accordance with the formula

$$\alpha - 1 = \frac{\ln \beta - \ln \beta_0}{\ln x},$$

where β_0 is the isotopic ratio of the heavy O^{18} isotope in the oxygen of natural composition and β is the same ratio in the oxygen remaining. The isotopic ratio is expressed as follows in conformity with the accepted nomenclature:

$$\beta = \frac{c}{1-c},$$

where c is the relative content of the heavy isotope in oxygen samples (isotopic concentration). The designation c_0 was adopted for the isotopic concentration of the natural composition. Thus, β, β_0, and x (the molar fraction of the light component in the residue) are found from the experimental data; and the value of the molar fraction of the light component is determined from the formula

$$x = \frac{(100-p)(1-c)}{100(1-c_0)};$$

the frequency of separation $\underline{n}$ is evaluated in accordance with the formula

$$n = \frac{\ln \beta_0 - \ln \beta}{\ln \alpha}.$$

Figures 2 and 3 list the experimental results from ascertaining the value of the separation coefficient α in electrosynthesis of ozone. Figure 3 shows the process in time of oxygen-ozone conversion. The curve of the dependence of $\underline{p}$ on time reflects the natural decrease in the velocity of oxygen-ozone conversion when the process is tending toward saturation.

In step with the oxygen-ozone conversion the remaining oxygen becomes poor in the heavy isotope O^{18} (Figure 2). Figure 2 also shows the dependence of the separation coefficient α on the degree of oxygen-ozone conversion. At a degree of conversion of from 45 to 90% the separation coefficient, within the experimental limits of error, remains constant and does not depend on $\underline{p}$. The average value of the separation coefficient turned out to be 1.08.

We may assume that the separation of isotopes in electrosynthesis of ozone results from an exchange between oxygen and ozone as well as from the rupture and formation of new chemical bonds in the conversion of oxygen into ozone. During this, the isotopic effect from the synthesis will by nature not depend on the degree of oxygen-ozone conversion.

The isotopic effects of the rupture and formation of chemical bonds are described in the literature [2, 3]. They are rather significant in their value for the light elements and amount to 8-10% and above.
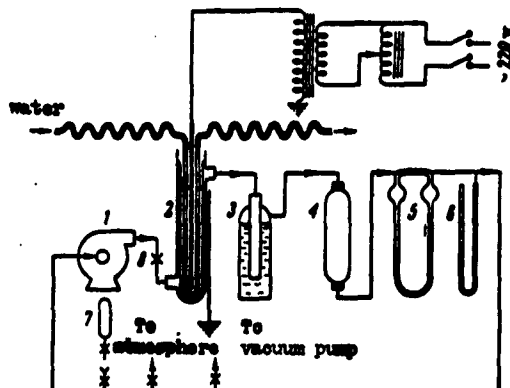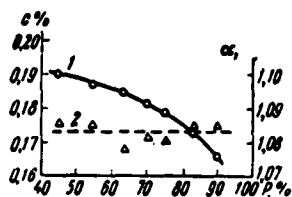
Fig. 1.   Diagram of setup.

Fig. 2.   Dependence of
separation coefficient
and of O^{18} concentra-
tion in residue on degree
of conversion.   1) Change
of O^{18} concentration in
residue, 2) separation
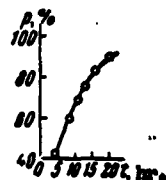coefficient.

Fig. 3.   Dependence of
degree of oxygen-ozone
conversion on time.

REFERENCES

1.   I. A. Semiokhin, G. M. Panchenkov.   Zh. Fiz. Khimii, 33,
1933, 1959.

2.   R. Nakane.   Repts. Scient. Res. Inst., 34, 203, 1958.

3.   The Use of the Trace-Atom Method in Chemistry.   A collection.
Izd. inostr. lit., P. 111, 1959.

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